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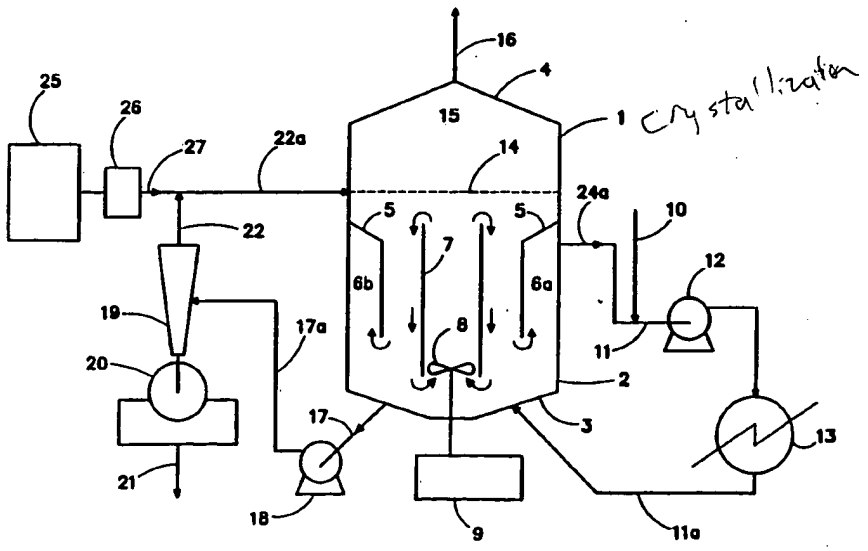

(57) Abstract

In a continuous crystallization process employing an evaporative draft tube baffle (DTB) crystallizer apparatus to produce crystal product, the improvement which is feeding at constant rate to the body of slurry a suspension of crystals in a solution at a temperature no greater than the operating temperature of the DTB crystallizer vessel, said suspension of crystals comprising solute and 6 to 24 % by volume, based on total volume of the suspension, of crystals with at least 35 % of the crystals larger than 14 mesh (1.2 mm) in size, in an amount whereby the weight of crystals is 4 to 25 percent of the weight of the product withdrawn, whereby cycling in the particle size distribution of the product withdrawn is reduced and rate of production of granular size crystals is increased.

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PROCESS FOR CRYSTALLIZATION IN A DRAFT TUBE BAFFLE CRYSTALLIZER

BACKGROUND OF THE INVENTION

1. Field of the Invention.

This invention relates to a process for crystallization in a draft tube baffle crystallizer wherein cycling in the particle size distribution of the product withdrawn is reduced and the rate of production of granular size crystals is increased.

2. Description of Related Art.

Many useful products are produced by crystallization from aqueous solution. It is desirable to produce large particles for both commercial and process benefits. This is particularly true for materials which are used in the fertilizer applications, such as ammonium sulfate, potassium chloride, and potassium sulfate. The trend of modern agriculture is to employ bulk blends, i.e., mixtures of crystals of individual fertilizers. Granular size crystals, i.e., large crystals of greater than 1.7 mm, command a premium price because they can be applied more uniformly and segregate less from crystals of other components of the bulk blends. When the crystallizer produces a preponderance of large crystals, removal of mother liquor is expedited and the drying and screening operations are more efficient.

Production of large crystals has been made easier with the introduction of the draft tube baffle crystallizer (DTB). The design of this crystallizer is described in U.S. Patent 3,873,275. The problem with the DTB crystallizer is the tendency to cycle, that is, exhibit a large time dependent variation in the crystal size distribution. Although the DTB crystallizers can produce a high percentage of their production as crystals of size greater than 1.7 mm when at the high points of the cycle, considerably less is made at the low points. There is also production of considerable

quantities of fine crystals at these low points. These wide variations in crystal size distribution are undesirable because there is loss of premium priced large crystals, introduction of non-uniformity in product size caused by segregation in storage piles and difficulties in screening.

U.S. Patent 4,263,010 teaches a dynamic control method and apparatus for obtaining a uniform particle size. A light scattering particle size analyzer is utilized to analyze a preconditioned classified sample of the crystal population of the crystallizer. A data analyzer then converts the signals from the particle analyzer into control signals to manipulate various process control variables such as fines removal rate, feed rate, pH adjustment, mixing rate and/or seed addition.

Japanese Patent publication no. 150127 describes a method for making large crystals of ammonium sulfate from a DTB crystallizer. This document teaches monitoring of slurry density, stirrer motor current, the height of the crystal bed under the baffle in the elutriation chamber and the crystal size distribution. Withdrawal of slurry from the crystallizer is alternately increased and decreased to keep the particle size distribution between an upper limit (onset of the crest in the cycle) and a lower limit (the onset of a fines shower). Effectively, this method does not eliminate cycling; but reacts to it to increase total production of large crystals. Data in the publication show that although the production of crystals above screen size 12 (1.4 mm) is reasonably stabilized; the more desirable crystals above size 9 (2.00 mm) still varies from about 35 to about 90%. The publication also teaches wet screening of the slurry withdrawn, and return of fine crystals with mother

liquor to the crystallizer. Since the withdrawal rate varies, it is inferred that the addition rate of these fine crystals is not constant.

Japanese Patent publication no. 51970 teaches addition of 1-20% fine crystals (based on clear saturated feed solution) of ammonium sulfate of a desired shape to a cooling crystallizer to produce an increase of large crystals of the desired shape. The fine crystals are defined as those below 20 mesh (0.85 mm). It is preferred to keep the amount of seed below 20% or the crystal size will be too small. The publication is somewhat confusing since the example shows that addition of 1% feed produces no increase in crystals above 12 mesh (1.4 mm), and only addition of 10% seed crystals increases the 12 mesh from 39 to 44%. The publication also teaches that if the seed exceeds 20 mesh (0.6 mm), the crystals will be too large. This is difficult to understand because even if all of the ammonium sulfate formed by cooling the clear solution precipitated on the seed, the size should only grow to about that of a 16 mesh crystals (1.0 mm).

SUMMARY OF THE INVENTION

In a continuous crystallization process employing an evaporative draft tube baffle (DTB) crystallizer apparatus to produce crystal product comprising

(a) introducing a clear feed solution containing dissolved solute to a body of slurry which comprises crystal particles in a solution in a vessel of the DTB crystallizer apparatus;

(b) maintaining conditions in said vessel for establishing super saturation in said slurry body to induce crystallization therein;

(c) circulating said body of slurry in a predetermined flow path in said vessel at a flow rate

sufficient to maintain said crystal particles in suspension;

(d) segregating a portion of said slurry body in a plurality of elutriation chambers;

(e) withdrawing a stream of crystal particles below a predetermined size and slurry liquid from each of said elutriation chambers through an outlet adjacent an upper end thereof, removing the crystal particles in the stream by dissolution and thereafter returning the stream to the body of slurry in the vessel; and

(f) continuously removing product crystals from the DTB crystallizer apparatus;

the improvement comprising

(g) feeding at constant rate to the body of slurry a suspension of crystals in a solution at a temperature no greater than the operating temperature of the DTB crystallizer vessel, said suspension of crystals comprising solution and 6 to 24% by volume, based on total volume of the suspension, of crystals with at least 35% of the crystals larger than 14 mesh (1.2 mm) in size, in an amount whereby the weight of crystals is 4 to 25 percent of the weight of the product withdrawn in step (f); whereby cycling in the particle size distribution of the product withdrawn is reduced and rate of production of granular size crystals is increased.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 represents a schematic diagram of apparatus for employing the process of the invention.

Fig. 2 represents cyclic behavior without addition of the suspension for successive shifts of production.

Fig. 3 represents the stable behavior obtained by the process of this invention with the

addition of the suspension for successive shifts of production.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The crystallization apparatus utilized in this invention is similar to that in both design and operation as that described in the Bennett Patent US 3,873,275. This apparatus has become known in the crystallization industry as a draft tube baffle crystallizer (DTB). A description of a typical apparatus and its normal operation are given below. The description and examples are written for crystallization of ammonium sulfate; but the same type of apparatus may be used for crystallization of potassium chloride, potassium sulfate, sodium chloride and other crystalline materials.

A simplified diagram of apparatus is shown in Figure 1.

The crystallization vessel generally designated by the numeral 1 consists of a cylindrical section 2 to which is attached a tapered bottom section 3 and a domed top section 4. A funnel-shaped baffle 5 defines two elutriation chambers 6a and 6b via vertical supports which are not shown. The number 7 designates a draft tube. Circulation of crystal slurry is provided by a propeller 8 mounted to a shaft and drive 9. Flow is up the draft tube and down along its exterior; and is of sufficient velocity to suspend the crystals in the vessel.

Concentrated ammonium sulfate feed solution from line 10 which is drawn into line 11 via the pump 12 is heated in heat exchanger 13 and enters the vessel via line 11a. It is mixed with circulating slurry within the vessel and propelled upward through the draft tube 7 via the movement of propeller 8. Evaporation of solvent water takes place close to the

liquid level 14 induced by a vacuum created in the vapor space 15. Water vapor is removed via line 16. Evaporation of sufficient water causes the saturation limit of ammonium sulfate to be exceeded. This supersaturation is relieved either by deposition of newly-formed ammonium sulfate on existing crystals which is desirable or by formation of new fine ammonium sulfate crystals often referred to as nuclei, which is undesirable because it leads to smaller-sized crystals.

Crystal slurry is removed via line 17 by the suction of pump 18 and discharged to a thickener 19 by line 17a. The thickener is normally a cyclonic separator. The thickened crystal slurry is discharged to a centrifuge 20 where crystals are separated from mother liquor. The wet crystals are discharged via line 21 to a dryer (not shown), then screened to the appropriate product size.

The overflow of thickener 19 which consists of crystals and saturated solution is returned to the crystallizer close to the liquid level 14 by lines 22 and 22a.

Nuclei and small crystals with mother liquor are removed from the crystallizer via the elutriation chambers 6a and 6b formed by the baffle 5, and are conveyed to line 11 by lines 24a and 24b (not shown for simplicity) where this fines slurry mixes with fresh feed from line 10 and the crystals subsequently are dissolved by heat supplied by heat exchanger 13.

A typical large DTB crystallizer useful for this invention is about 50 ft. tall and 24 ft. in diameter and has volume of about 100,000 gallons. Circulation up the draft tube is about 100,000 gallons per minute. The circulation through the external fines dissolving circuit provided by pump 12 is about 10,000 gallons per minute.

The present invention provides an improved crystallization process in which cycling in the size distribution of product crystals is reduced and the production of crystals larger than size 10 Tyler mesh (1.70 mm) is improved. This method consists of adding at constant rate to the crystallizer vessel a suspension of crystals in essentially saturated solution from some external source designated 25 on Figure 1. Flow is controlled by the flowmeter 26. The drawing shows the suspension enters the crystallization apparatus via line 27 to line 22A, the thickener overflow line, which enters the crystallization vessel 1 close to the liquid level 14. This has been done for simplification. It should be understood that the suspension could enter the vessel directly at some other point close to the liquid level 14 or close to the bottom inlet to the draft tube 7 via appropriate piping.

We have found that both the size and quantity of the crystals are important. It was found that the crystals in the suspension must be a mixture of medium sized crystals (14 to 10 mesh) and smaller sized (below 14 Tyler mesh). For effective operation, the suspension of crystals should contain 6-24% by volume, preferably 12-24%, of crystals with at least 35%, preferably 35-85%, of the crystals larger than 14 mesh (1.2 mm) in size. Additionally, it is preferred that no greater than 15% of the crystals are larger than 10 mesh (1.7mm). The suspension of crystals in a solution is added in an amount whereby the weight of crystals is 4 to 25%, preferably 8 to 20%, of the weight of the product which is withdrawn from the DTB crystallization apparatus via line 21. The temperature of the feed suspension should be no greater than, preferably at least 10°C lower than, the operating

temperature of the DTB crystallizer vessel.

Example 1

In the typical operation of the evaporative DTB crystallizer, the vessel is about 24 feet in diameter and is about 50 feet tall. The capacity is about 100,000 gallons. Clear ammonium sulfate solution (43% solution) is fed to the crystallizer operating at 80°C. Water is removed such that the production rate of crystals is 1310 lbs/min. The percent crystals in the slurry circulating in the vessel is 30% settled volume (about 17% crystals by volume). The percent of crystals of size greater than Tyler 10 mesh are given in Figure 2 for several successive shifts of production. The cyclic behavior is illustrated in Figure 2.

Example 2

The equipment of Example 1 is utilized except that 588 lbs/min of a suspension of 22.2 parts ammonium sulfate crystals in 77.8 parts of 46.6% ammonium sulfate solution is fed continuously at 60°C to the liquid level of the DTB crystallizer which operates at 80°C. The size distribution of crystals in the suspension is 1% 8 x 10 Tyler mesh (2.36 x 1.70 mm), 35% 10 x 14 Tyler mesh (1.70 x 1.40 mm); and 64% below 16 mesh (1.40 mm). The flow of clear 43% solution is reduced such that 1380 lb/min. of ammonium sulfate are withdrawn from the crystallizer. The percent of crystals greater than Tyler 10 mesh are shown in Figure 3 for several successive shifts. Comparison of Figure 3 with Figure 2 demonstrates the remarkable reduction in cycling of the particle size distribution of the product withdrawn from the process of the invention.

WE CLAIM:

1. In a continuous crystallization process employing an evaporative draft tube baffle (DTB) crystallizer apparatus to produce crystal product comprising

(a) introducing a clear feed solution containing dissolved solute to a body of slurry which comprises crystal particles in a solution in a vessel of the DTB crystallizer apparatus;

(b) maintaining conditions in said vessel for establishing super saturation in said slurry body to induce crystallization therein;

(c) circulating said body of slurry in a predetermined flow path in said vessel at a flow rate sufficient to maintain said crystal particles in suspension;

(d) segregating a portion of said slurry body in a plurality of elutriation chambers;

(e) withdrawing a stream of crystal particles below a predetermined size and slurry liquid from each of said elutriation chambers through an outlet adjacent an upper end thereof, removing the crystal particles in the stream by dissolution and thereafter returning the stream to the body of slurry in the vessel; and

(f) continuously removing product crystals from the DTB crystallizer apparatus;

the improvement comprising

(g) feeding at constant rate to the body of slurry a suspension of crystals in a solution at a temperature no greater than the operating temperature of the DTB crystallizer vessel, said suspension of crystals comprising solution and 6 to 24% by volume, based on total volume of the suspension, of crystals with at least 35% of the crystals larger than 14 mesh (1.2 mm) in size, in an amount whereby the weight of crystals is 4 to 25 percent of the weight of the

product withdrawn in step (f); whereby cycling in the particle size distribution of the product withdrawn is reduced and rate of production of granular size crystals is increased.

2. The process of claim 1 wherein said suspension of crystals comprises 12 to 24% by volume of crystals.

3. The process of claim 1 wherein said suspension comprises crystals with 35 to 85% of the crystals larger than 14 mesh (1.2 mm) in size and no greater than 15% of the crystals larger than 10 mesh (1.7 mm).

4. The process of claim 3 wherein said suspension of crystals comprises 12 to 24% by volume of crystals.

5. The process of any of claims 1, 2 or 3 wherein said suspension of crystals in a solution is fed in an amount whereby the weight of crystals is 8 to 20 percent of the weight of the product withdrawn in step (f).

6. The process of claim 4 wherein said suspension of crystals in a solution is fed in an amount whereby the weight of crystals is 8 to 20 percent of the weight of the product withdrawn in step (f).

7. The process of claim 6 wherein the suspension of crystals is fed in step (g) to the body of slurry at a point at or adjacent to the liquid level in the DTB crystallizer vessel.

8. The process of any of preceding claims 1-7 comprising the continuous crystallization of ammonium sulfate.

9. The process of any of preceding claims 1-8 wherein the suspension of crystals in step (g) is at a temperature at least 10°C lower than the operating temperature of the vessel.

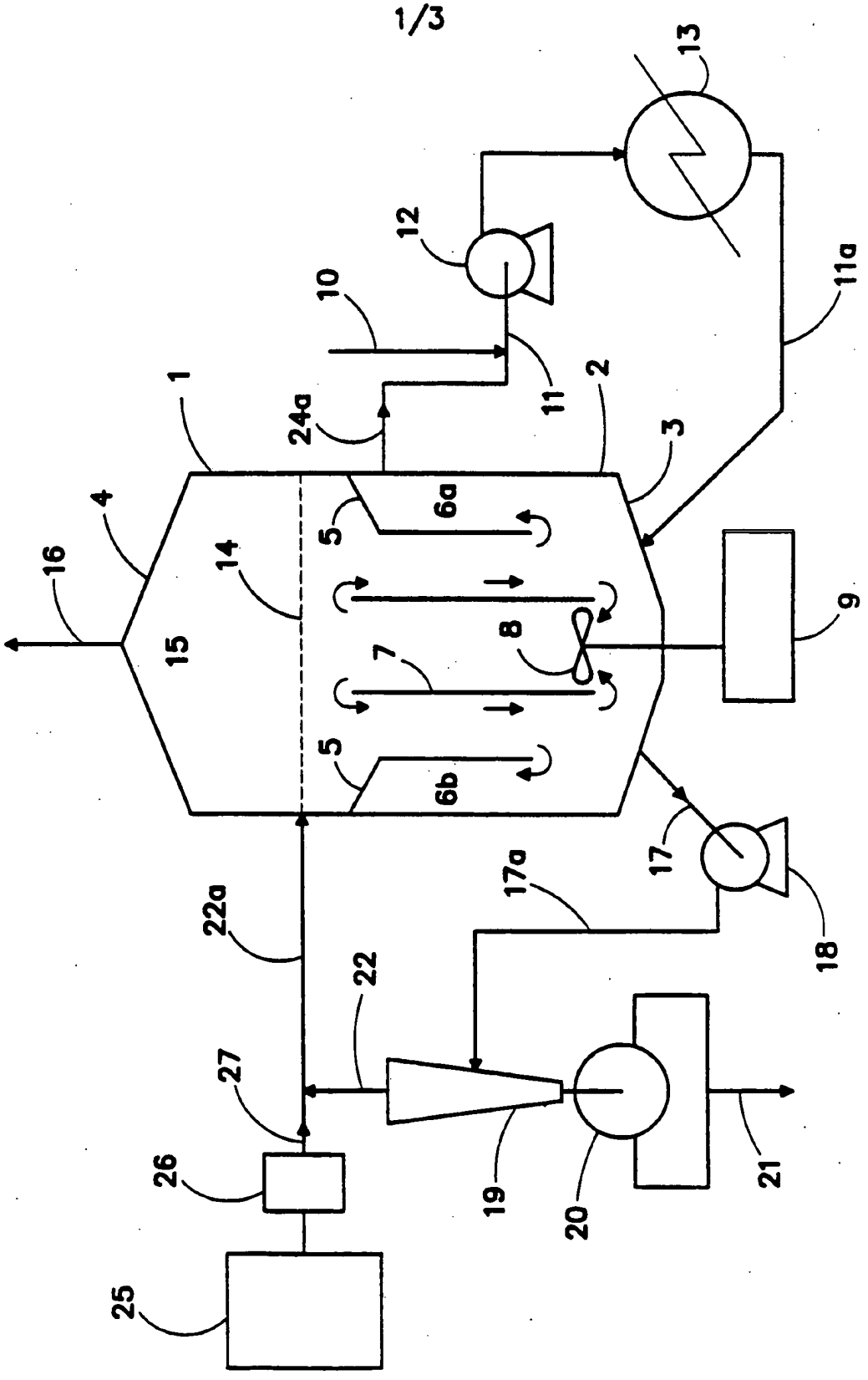
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FIGURE 1

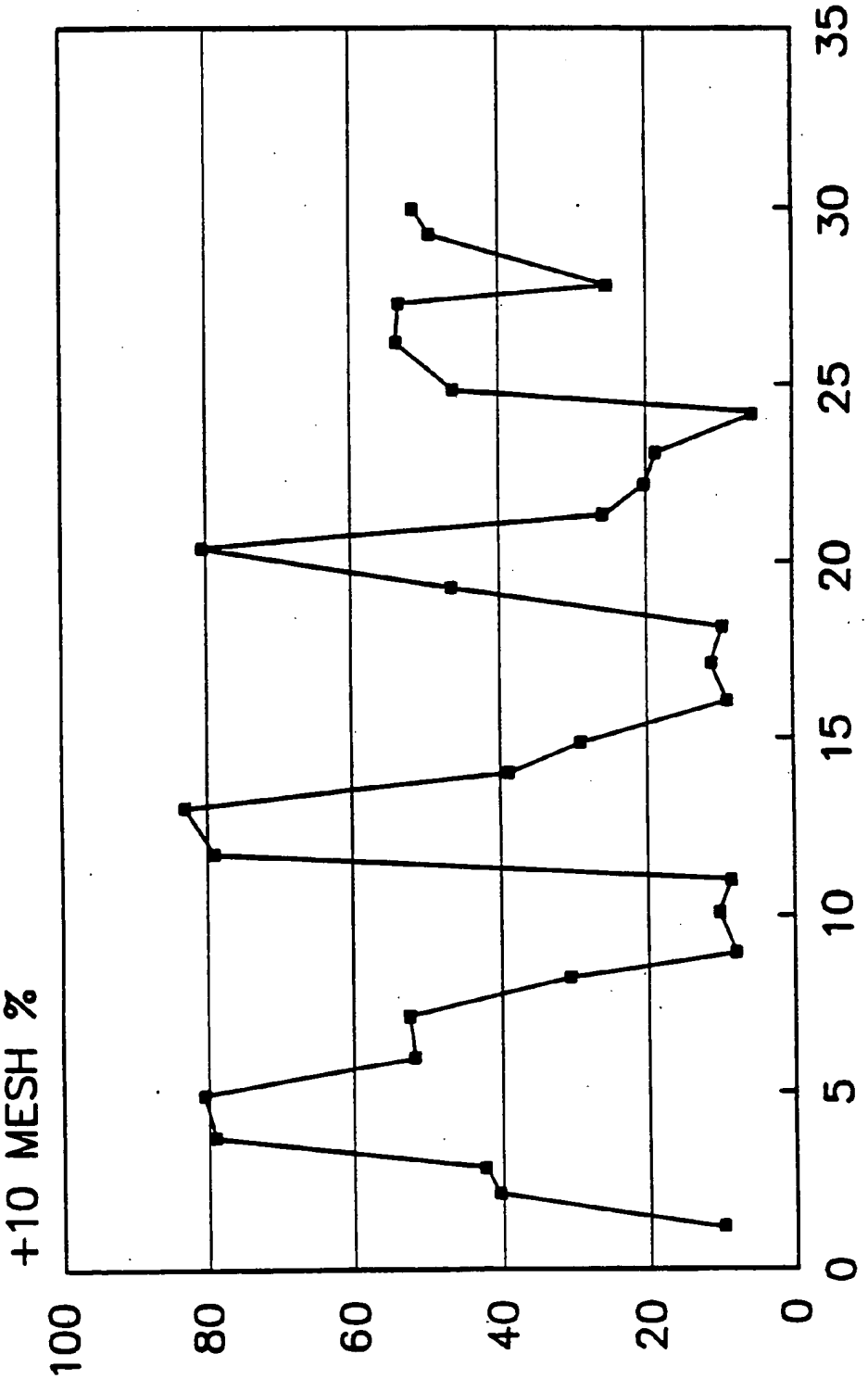

FIGURE 2

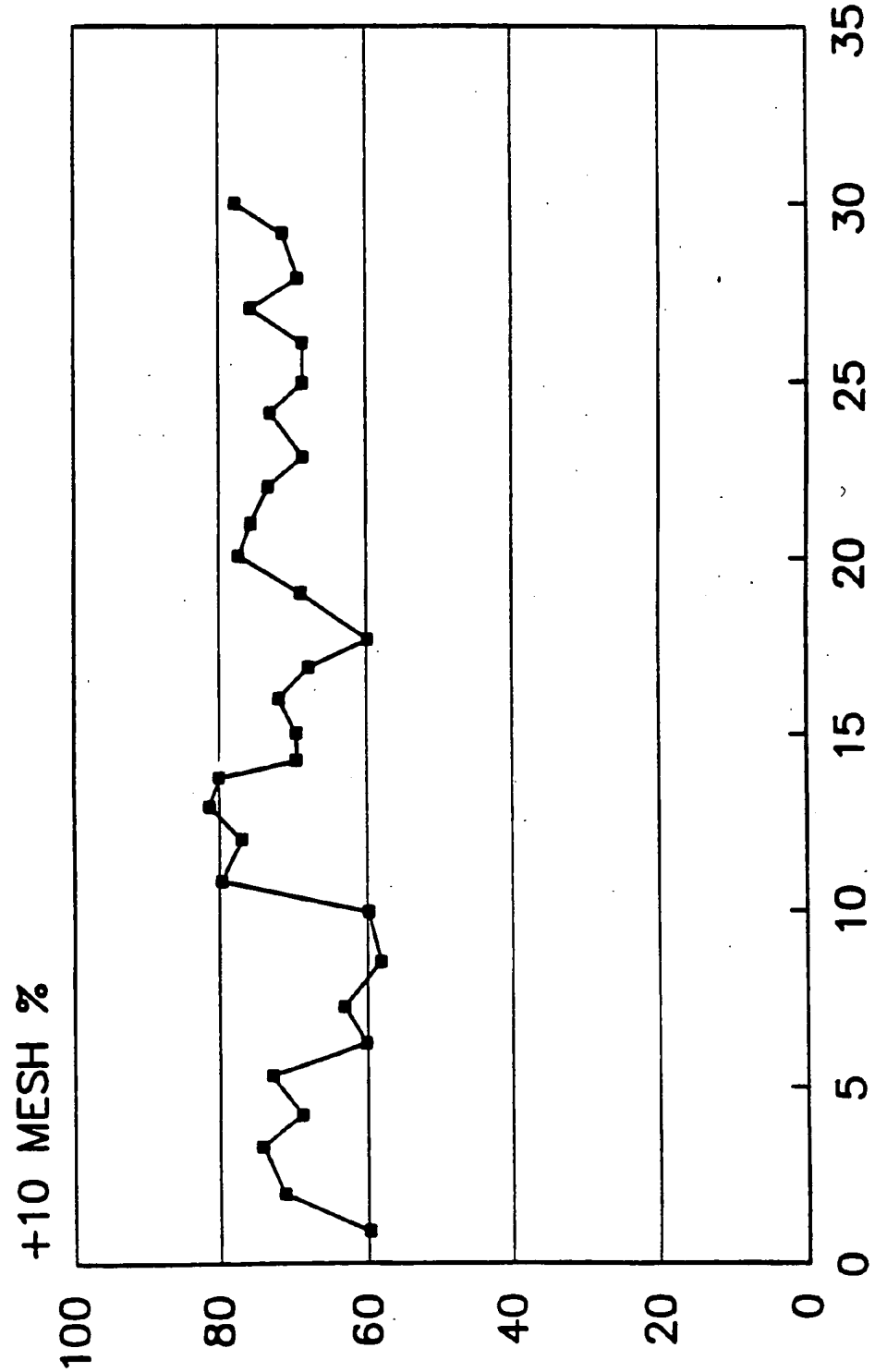

FIGURE 3

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 93/01132

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 B01D9/00

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	B01D

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
A	US,A,3 873 275 (R.C. BENNET) 25 March 1975 cited in the application see the whole document	1
A	US,A,3 628 919 (W.D. BEAUCHAMP ET AL.) 21 December 1971 see abstract see column 2, line 64 - column 3, line 47 see column 4, line 70 - column 5, line 27; figure	1,6
A	US,A,2 346 517 (J. H. THOMPSON) 11 April 1944 see column 2, line 76 - column 3, line 32; claims; figure	1
A	US,A,3 071 447 (T.G. BERNHARDI) 1 January 1963	

° Special categories of cited documents : [10]

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"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
11 JUNE 1993	24. 06. 93
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	PLAKA T.

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9301132
SA 70758

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
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US-A-3628919	21-12-71	None	
US-A-2346517		None	
US-A-3071447		None	